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SYNTHESIS AND CHARACTERIZATION OF HIGH ENERGY POLYMERS.(U)
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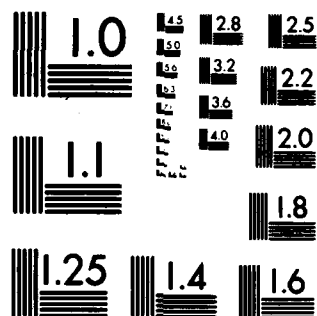
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Synthetic procedures for selective nitromercuration via phase transfer
catalysis have been developed for usage with water insoluble poly(butadiene),
poly(isoprene), and carboxyl terminated butadiene acrylonitrile copolymers.

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ANNUAL SUMMARY REPORT

SYNTHESIS AND CHARACTERIZATION OF HIGH ENERGY POLYMERS

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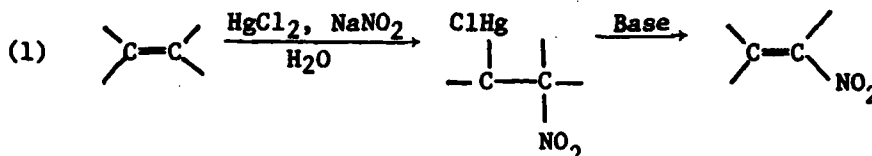
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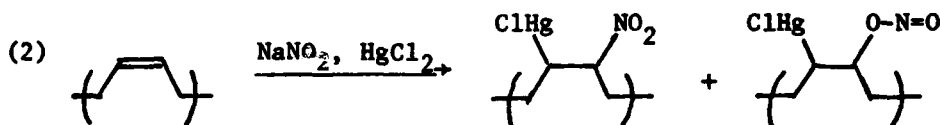
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INTRODUCTION

The goal of this years effort was to develop a method for mild selective nitration of olefinic polymers. The Corey-Estreicher¹ nitromercuration-demercuration method (equation 1) was studied in detail.



Olefinic polymers fail to undergo nitromercuration under the Corey conditions owing to their insolubility in the aqueous nitromercuration reagent. This problem was overcome through use of quarternary ammonium cations as phase transfer catalysts. A second problem associated with nitromercuration is the formation of nitrite ester at the expense of nitro functionality (equation 2)

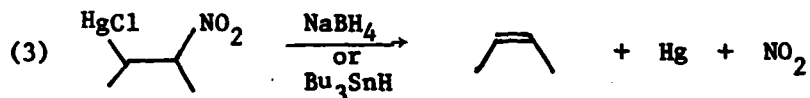


Presence of nitrite ester causes severe problems in the demercuration step. We have discovered that nitrite ester formation can be virtually eliminated by conducting the nitromercuration reaction in methylene chloride in the presence of phase transfer catalyst and a small quantity of added water. These findings are the subject of a paper accepted for publication in the Journal of Polymer Science (see bibliography).

We have also found that selective nitromercuration in methylene chloride can be achieved using crown ethers. Furthermore, the phase transfer catalysis technique offers advantages in rate and selectivity over the original Corey-Estreicher method for nitromercuration of water-insoluble mono-olefins such as 1-octadecene.

Demercuration of polymers which contain both nitro and nitrite ester functions is complicated by a nitrite ester catalyzed oxidation of nitro functions to carbonyl groups. Base promoted demercuration of polymer which contains substantial nitrite ester results in loss of nitro functionality and production of a dark insoluble product. Preliminary experiments with nitromercurated poly(butadiene) which is nearly nitrite-free have given partial demercuration with little carbonyl formation.

Several other demercuration procedures have been investigated. Reductive demercuration using hydrogen sulfide or β -mercaptoethanol failed. Reductive demercuration using sodium borohydride or tri-*n*-butylstannane give mostly olefin according to equation 3.



Conditions to improve the yield of nitro compounds from these reactions are being sought.

In summary, an efficient selective nitromercuration reaction has been developed. Base promoted demercuration currently appears to be the most promising way to complete the synthesis and is being studied.

DETAILED ACCOUNT OF TECHNICAL ACTIVITIES

I. Nitromercuration of Olefinic Polymers

A. Methods and Materials

Polymers studied were poly(cis-1,4-butadiene), (Natsyn 2200-Goodyear, $\bar{M}_n = 2 \times 10^5$), poly(cis-butadiene) (from Snam Progetti, 98.0% cis-1,4) and a carboxy-terminated poly(butadiene-co-acrylonitrile) (B:AN = 9:1, $\bar{M}_n = 3600$) supplied by Dr. Carl Gotzmer, Naval Surface Weapons Center, Dahlgren, VA.

Nitromercuration was monitored by infrared spectroscopy (-NO_2 antisym. N-O stretch at 1545 cm^{-1}), analyses for mercury and by total weight gain of the polymer. The phase transfer catalyst used in most experiments was tetra-n-butylammonium bisulfate (TBAB).

B. Findings

Olefinic polymers did not react with aqueous $\text{HgCl}_2/\text{NaNO}_2$ reagent.

Solution of polymer in an organic solvent to give a two-phase system resulted in slow reaction. Under these conditions the nitromercuration rate was dependent on $[\text{HgCl}_2]$ but not on $[\text{NaNO}_2]$. Thus, the mechanism involves rate

Table I determining attack of Hg(II) on the olefinic bond. Table I gives results of this initial survey.

able II,III Tables II and III show results of further experiments. First, the results in Table II show that phase transfer catalysis in a two-phase $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ system accelerates nitromercuration but gives substantial nitrite ester (runs 1 and 2). Phase transfer catalysis in methylene chloride alone (runs 4 and 6) gave higher rates and better selectivity. Nitromercuration in mixtures of DMF and methylene chloride were found to be selective but relatively slow.

Table III shows the results of our study of the effect of small amounts of water on nitromercuration. The reaction rate is optimized by addition of 1.0 mL water/100 mL methylene chloride. Selectivity reaches a maximum on addition of only 0.2 mL water and is unaffected by addition of larger amounts. The function of phase transfer catalyst under these conditions is to transfer nitrite ion from insoluble sodium nitrite into methylene chloride in the form of soluble tetrabutylammonium nitrite ion pairs. The crown ether 15-Crown-5 works as well as TBAB but is more expensive and offers no advantage.

Table I
Initial Survey of Nitromercuration

Run	Conditions		Time (hr)	Nitro ^b Absorption A ₁₅₄₅ /A ₁₄₅₀	Percent ^c Theoretical Mercuration
	Substrate ^a	Solvent(s)			
1	PI	H ₂ O	24	0.0	
2	PI	H ₂ O/THF(1:1)	28	0.0	
3	PI	H ₂ O/p-xylene	24	0.1	
4	PI	H ₂ O/CH ₂ Cl ₂	24	0.3	
			141	0.9	3
5	PI	H ₂ O/methyl- cyclohexane	25	0.2	
			258	1.3	12
6	BAN	H ₂ O/CH ₂ Cl ₂	96	2.3	10
7	PB	DMSO	50	0.0	
8	PB	DMF	50	0.0	

^aPI = cis-poly(isoprene); PB = cis-poly(butadiene); BAN = carboxy-terminated copoly(butadiene-co-acrylonitrile) (9:1), $M_n = 3600$.

^bRatio of infrared absorption intensities at 1545 and 1450 cm^{-1} . See experimental section for details.

^cBy elemental analysis.

Table II
Phase Transfer Catalysis Effects on Nitromercuration

Run	Substrate	Solvents	PTC ^a	Time (hr)	Insoluble Polymer Fraction	Nitro ^b A ₁₅₄₅ / A ₁₄₅₀	Nitrite/ Nitro ^b A ₁₆₄₀ / A ₁₅₄₅	% ^c Theoretical Mercuration
1	PB	CH ₂ Cl ₂ /H ₂ O	no	314	no	2.2	0.6	13
2	PB	CH ₂ Cl ₂ /H ₂ O	yes	24	no	1.8	0.2	
				50	no	1.6	0.6 ^d	
3	PB	CH ₂ Cl ₂	no	120	no	0.9	0.4 ^d	
				216	no	2.2	0.4 ^d	
				312	no			
4	PB	CH ₂ Cl ₂	yes	90	yes	3.4	0.2	60
5	PI	CH ₂ Cl ₂ /H ₂ O	no	312	no	1.4	0.7	
6	PI	CH ₂ Cl ₂	yes	96	yes	1.6	0.5	

^a10 Mole % tetrabutylammonium bisulfate.

^bTotal crude product. Ratio of infrared absorbances at indicated wavelengths (see experimental).

^cBy elemental analysis.

^dProducts exhibited substantial carbonyl absorption.

Table III

Effect of Water on Phase Transfer-Catalyzed Nitromercuration
of cis-Poly(butadiene) in Methylene Chloride

Water Added (mL/100 mL CH ₂ Cl ₂)	Time (hr)	Fraction ^a	Weight (g) ^b	% Nitro- ^c mercuration	Nitro ^d A1545/ A1450	Nitro/ ^d Nitrite A1640/ A1545
Anhyd	8	soluble			0.2	0.7
	52	soluble			1.1	0.6
	52	insoluble	0		-	-
0 ^e	8	soluble			1.2	0.5
	52	soluble	2.76		2.2	0.2
	52	insoluble	~0.04	30	4.3	0.1
0.2	8	soluble			3.4	0.3
	52	soluble	3.04		5.4	0.1
	52	insoluble	0.38	41	5.4	0.1
0.4	8	soluble			4.5	0.1
	10	soluble	2.65		6.07	0.1
	10	insoluble	0.34	28	6.11	0.1
	27	soluble	2.73		6.14	0.1
	27	insoluble	0.78	42	6.62	0.1
	52	soluble	0.48			
	52	insoluble	4.39	66		
1.0	8	soluble			5.2	0.1
	24	soluble	3.63		5.2	0.1
	24	insoluble	0.22	48	5.9	0.1
	52	soluble	0.32			
	52	insoluble	4.85	72	5.2	0.1

Table III (cont.)

2.0	8	soluble			2.7	0.3
	52	soluble	~3		4.5	0.1
	52	insoluble	~0.4	~40		
5.08	7	soluble			2.7	0.4
	52	soluble	3.18		5.8	0.1
	52	insoluble	<0.2	39		
10.08	8	soluble			1.45	0.4
	27	soluble			1.9	0.4
	52	soluble	2.60		3.8	0.13
		insoluble	0.08	29		

^aSolubility in methylene chloride.

^bWeight of starting PB = 1.08 g

^cPercent of theoretical nitromercuration according to total weight gain, for soluble plus insoluble product

^dRatio of infrared absorbances at indicated wavelengths, see experimental section for detail

^eNo precautions taken to exclude adventitious water

^fInsoluble fractions ~0.04 g

^gA separate aqueous phase is apparent

C. Optimum Phase Transfer Catalyzed Nitromercuration Procedure

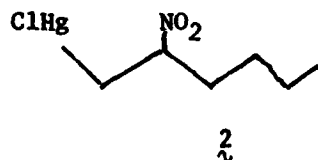
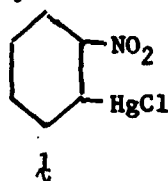
Poly(cis-butadiene) (1.08 g, 20 mmole of olefin) was dissolved in 100 ml of CH_2Cl_2 . To this solution were added HgCl_2 (20 mmole), NaNO_2 (40 mmole), and tetrabutylammonium bisulfate (2 mmole). Additional water (1.0 ml) was added at this point. The reaction vessel was stoppered and the reaction mixture was stirred magnetically at ambient temperature. At the end of the reaction, the liquid phase was decanted into a separatory funnel and the solid residue was washed with CH_2Cl_2 (3 x 10 mL). The combined CH_2Cl_2 phase was washed with water (4 x 200 ml). This solution was dried (Molecular Sieve 3A) and evaporated to give soluble nitromercurated polymer. Washing the insoluble residue (95% ethanol, 3 x 5 mL; water, 3 x 5 mL; 95% ethanol, 1 x 5 mL) and drying in vacuum gave the insoluble polymer fraction as a white solid.

II. Demercuration of Nitromercuri Intermediates

A. Base Promoted Demercuration of Low Molecular Weight Model Compounds.

(Table IV)

Compounds studied were the nitromercuri derivatives of cyclohexene and 1-hexene (**1** and **2** respectively).



Demercuration of **1** with 2.5 N aqueous NaOH gives 1-nitrocyclohexene rapidly in high yield. An infrared spectrum of the total crude product shows no evidence for side products. Demercurations with amines (triethylamine and diazabicycloundecene, DBU) proceed more slowly and do not appear to go to

Table IV
Base-Promoted Demercuration of Model Compounds

Compound	Base (eq)	Time(min)	IR Absorption of Product			Recovered Hg
			Carbonyl ^a	Nitrite ^b	Sat-NO ₂ ^c Unsat-NO ₂ ^d	
1	DBU (1.0)	5	w-m	w-m	s	13%
Prod. from reaction above	DBU (1.0)	5	w-m	w-m	s	none
1	DBU (2.0)	30	w	m-s	s	--
1	NEt ₃ (5)	10	-	vw	m	--
1	2.5 M NaOH (4)	1	-	-	vs	84%
1	2.5 M NaOH (4)	45	-	-	vs	--
2	DBU (1)	2	-	s	m	--
2	NEt ₃ (excess)	2	-	-	s	>40%
Nitromercuri 1,5-heptadiene	2.5 M NaOH (excess)	>30		m-s	m-s	--

^a IR absorption at ca. 1710 cm⁻¹; w = weak, m = medium, s = strong.

^b IR absorption at 1650 cm⁻¹.

^c IR absorption at 1550 cm⁻¹.

^d IR absorption at 1510 cm⁻¹.

completion easily. Products formed are less clean and there is preliminary evidence (smell and gas chromatography) for loss of NO_2 to give cyclohexene. In contrast, NEt_3 gave clean demercuration of 2 whereas DBU did not. The implication of these findings and of Corey's report is that the optimum base must be found for each individual case empirically.

B. Base Promoted Demercuration of Nitromercurate cPolymers

Conditions used to demercurate insoluble, highly-nitromercurated poly-(butadiene) are given in Table V. Rapid development of a gray color is evidence for formation of Hg^0 . The polymer remained insoluble all these reactions and could not be separated from the mercury. For this reason we have directed subsequent effort to demercuration of soluble polymers.

Results are presented in Table VI. Sodium hydroxide promoted demercuration of polymers does not proceed as cleanly as it does in the case of 1 (above). Broad IR absorptions are evidence for formation of a variety of functional groups, and loss of nitro functionality is apparent at longer reaction times. Emulsion formation was also a problem. Amine promoted demercuration has given more promising results. Treatment with amines causes separation of metallic mercury, and causes decrease of saturated nitro absorption at 1545 cm^{-1} and appearance of unsaturated nitro absorption at 1510 cm^{-1} in the IR. This reaction with DBU, the stronger base, is more rapid but also gives a product with stronger $-\text{OH}$, carbonyl and nitrite ester absorption in the IR. The polymers produced form uniform films which are transparent with a rust color.

Table V

Base Promoted Demercuration of Insoluble Nitromercurated Poly(butadiene)

<u>Sample</u>	<u>Base</u>	<u>Time (hr)</u>	<u>Solvent</u>
TK #25	2.5 <u>M</u> NaOH, TBAB ^a	24	CH ₂ Cl ₂
TK #25	2.5 <u>M</u> NaOH	12	Ethanol
TK #25	DBU	12	CH ₂ Cl ₂
TK #25	DBU	12	CH ₂ Cl ₂ /DMF (10/1)
TK #25	2.5 <u>M</u> NaOH	12	Water
TK #25	2.5 <u>M</u> NaOH	24	CH ₃ CN

^aTetrabutylammonium bisulfate phase transfer catalyst.

Table VI
Base-Promoted Demercuration of Soluble Nitromercurated
Polymers in Methylene Chloride

<u>Polymer</u>	<u>Base^a</u>	<u>Time</u>	<u>IR Absorption of Products</u>					<u>Hg^o</u>
			<u>-OH</u>	<u>C=O</u>	<u>-ONO</u>	<u>Sat-NO₂</u>	<u>Unsat-NO₂</u>	
Poly(butadiene) ^b	NEt ₃	10 min	w	w	m	s	m-s	yes
Poly(butadiene) ^b	DBU	2 min	s	w-m	m-s	m-s	s	yes
Poly(butadiene) ^b	2.5 <u>M</u> NaOH	2 min	(Broad absorption in OH and nitro regions) ^d					yes
BAN ^c	Et ₃ N	20 hr	s	m-s	s	s	w	yes
Product from reaction above	Et ₃ N	20 hr	s	m	s	m	-	yes
BAN ^c	2.5 <u>M</u> NaOH	>12 hr	w	m-s	m-s	m-s	m-s	yes
BAN ^c	2.5 <u>M</u> NaOH/ TBAB ^e	24 hr	s	m-s	s	s	shoulder	yes

^aExcess base used in all experiments.

^bTRS-III-33A.

^cTRS-I-6A.

^dIR absorptions were broad and extended across all indicated regions.

^eTetrabutylammonium bisulfate phase transfer catalyst.

References

1. E.J. Corey and H. Estreicher, J. Am. Chem. Soc., 100, 6294 (1978).
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